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The dependence of electrical transport of doped polyacetylenes on conjugation length has been a topic of debate in recent year [1-3]. We do not wish to comment on this issue specifically but rather on the synthetic approach of introducing sp^3 defects into polyacetyene through protonation [3-5] or alkylation [6] of the n-type derivative (n-PA). Specifically, we address the question of the randomness of the palcement of defects and its implications for carrier transport and other electronic properties. Our principal conclusion is one defect for every 10 carbons in polyacetylene. We base this conclusion on experimental results reported in the literature and our theoretical study.

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A comment on random vs. non-random defect placement in polyacetylene

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Introduction

The dependence of electrical transport properties of doped polyacetylenes on conjugation length has been a topic of debate in recent years [1-3]. We do not wish to comment on this issue specifically but rather on the synthetic approach of introducing sp^3 defects into polyacetyene through protonation [3-5] or alkylation [6] of the n-type derivative (n-PA). Specifically, we address the question of the randomness of the placement of defects and its implications for carrier transport and other electronic properties. Our principal conclusion is that relatively long conjugation lengths prevail even after introducing ca. one defect for every 10 carbons in polyacetylene. We base this conclusion on experimental results reported in the literature (see below) and our theoretical study (see next section).

There are two reasons why protonation or alkylation of n-PA, in our view, is likely to afford sp^3 defects which are not randomly situated on the polymer backbone. The first is that polyacetylene is semi-crystalline, and anticipated faster kinetics of reaction in the 'amorphous' phase would leave unscathed large segments of conjugation. The second, and likely more important, point is based on a thermodynamic argument, namely that conjugated sequences are more stable than conjugation-interrupted sequences. For example, the resonance energy of conjugated dienes obtained from heats of formation is roughly 3-4 kcal/mol [7]. However, even if protonation (say, using methanol) were to occur rapidly and randomly (kinetic control), the base generated upon protonation (e.g., CH_3O^-) can catalyze isomerization to the thermodynamic (conjugated) product. Dias and McCarthy [7] demonstrated that polybutadiene can be isomerized to poly(acetylene-co-ethylene), which was found to contain oligoacetylene units of up to 10 double bonds. The key point is that the $-CH_2CH_2-$'defects' in polybutadiene, in the presence of a base catalyst in this case, tend to cluster, as do the double bonds. The observation of increased conjugation length upon protonation of deprotonated butadiene/acetylene copolymers is in accord with this idea [8].

We note that 'doping' with electron acceptors presents another opportunity to attain long conjugation lengths through a series of hydride shifts, a well established concept in organic chemistry. A similar argument can be made for proton shifts upon n-type doping. The point is that the conjugation lengths of sp^3-interrupted polyacetylenes measured before doping may not be preserved upon doping, suggesting that in a really meaningful conjugation length/conductivity study one should measure conjugation lengths after doping and compensation.

Experimental data support the view that protonation or alkylation of n-PA results in 'clustering' of defects rather than their random incorporation. In particular, the visible spectrum [4,5] of the product of protonation of n-PA by methanol has a λ_{max} of ca. 620 nm, blue shifted compared with *trans*-polyacetylene (λ_{max}= 700nm) but nevertheless suggestive of fairly long conjugation lengths (longer, in fact, than pristine *cis*-polyacetylene, λ_{max}= 530 nm). The visible spectrum is inconsistent with the average conjugation length of ca. 5 C=C which might be inferred from the amount of sp^3 defects from elemental analysis. (A similar spectrum was obtained from alkylated n-PA. [6]) In fact, the visible spectrum exhibits characteristics of 'short' conjugated sequences only after performing the n-doping and subsequent methanol treatment three times. The alternative interpretation, namely the sp^3 defects are placed randomly and yet have little influence on optical properties, is intuitively untenable.

We now present the results of a theoretical study which indicate that the optical properties of polyacetylene containing $-CH_2-$ defects cannot be accounted for by inferring the presence of a predominance of short conjugation lengths.

Calculations

Band structure calculations on polyacetylene containing methylene units separated by a varying number of conjugated double bonds were performed using the valence effective Hamiltonian technique [8], included in the ChemLab II software package from Molecular Design Ltd. In one set of calculations, a single methylene group interrupted the conjugated double bonds; another set employed two adjacent methylenes as the 'defect.' The C-C and C=C bond lenghts were taken as 1.46 and 1.35Å, respectively, with a C-C-C bond angle of 124.9° for defect-free polyacetylene, and for portions of the chain not adjacent to the defects. MNDO calculations were performed to obtain optimized bond lengths and angles in the regions near the methylene units.

Results and Discussion

The results of the calculations on pristine polyacetylene compared well with those of Brédas, et al. [10,11]; small differences in band gap energy values reflect differences in geometrical parameters. Figure 1 shows that the $\pi-\pi^*$ transition (band gap) increases from 1.52 eV for pristine polyacetylene to about 2.5 eV when there are only 6 conjugated double bonds between defects.

Results of calculations of the distribution of conjugation lengths from the random placement of methylenes along a chain are shown, for example, in Table 1. The placement assured that adjacent defects were compatible with bond formation, that is, an even number of C atoms were between methylene defects. Values of F_n, the fraction of sequences with N uninterupted acetylene units, show that 80% of the conjugated segments have 6 double bonds or fewer. Only about 6% have greater than 10 conjugated bonds. The fraction F_W (defined in Table 1) is more meaningful in terms of mass or volume. Still, 76% of the polymer has 10 or fewer conjugated bonds; 50% has 6 or fewer. This total number of methylene units is well within the range found to afford high conductivity upon doping with AsF_5 [3]. Our observation that only a small fraction of conjugated segments had a small band gap is inconsistent with the small blue shift in the visible spectrum [4] recorded after protonation of n-type polyacetylene.

It should also be noted that as the conjugation length decreases, the band width of the highest occupied band narrows considerably from greater than 6 eV to less than 0.1 eV, indicative of a low carrier mobility.

These results support the notion that defects introduced by protonation or alkylation of n-type polyacetylene are <u>not</u> placed randomly. The defects cluster with the result that reasonably long conjugation lengths prevail. It is therefore not possible to infer anything about average conjugation lengths based solely on a knowledge of defect concentration.

Note added: S. Jeyadev and E. Cowell drew similar conclusions in a paper presented at the American Physical Society March (1988) meeting. Our results were given in a poster at that meeting.

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Table 1. Fraction of segments between defects have N or fewer conjugated double bonds.

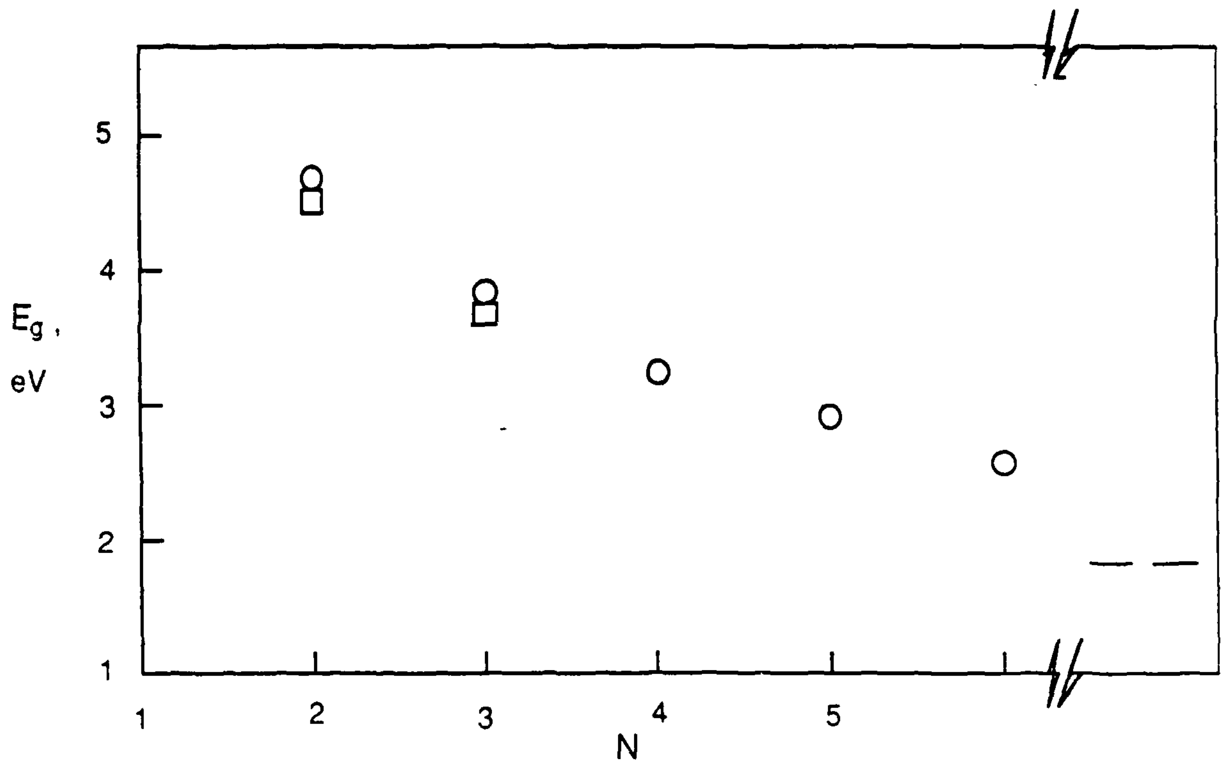
N	F_n	F_w
2	0.47	0.15
4	0.68	0.33
6	0.80	0.50
8	0.89	0.66
10	0.94	0.76

$$F_n = \sum_{0}^{N} n(N_i) \Big/ \sum_{\substack{\text{All} \\ \text{Segments}}} n(N_i)$$

$$F_W = \sum_{0}^{N} n(N_i)N_i \Big/ \sum_{\substack{\text{All} \\ \text{Segments}}} n(N_i)N_i$$

Figure Caption

Figure 1. Band gap energy vs. N, the number of conjugated double bonds between defects, for polyacetylene. The defects comprise single methylene units (squares) and two adjacent methylene groups (circles). The dashed line shows the calculated band gap energy for polyacetylene without defects.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